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AN EVALUATION OF TGS-ANSA PROCEDURE
FOR DETERMINATION OF NITROGEN DIOXIDE
IN AMBIENT AIR

Robert G. Fuerst, et al

National Environmental Research Center
Research Triangle Park, North Carolina

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Quality Assurance and Environmental Monitoring Laboratory

Program Element 1HA327

National Environmental Research Center
Office of Research and Development
U.S. Environmental Protection Agency
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ABSTRACT

A detailed method write-up describing the TGS-ANSA manual procedure for measurement of NO_2 in ambient air was developed. The method involves sampling for 24 hours with a restricted-orifice bubbler immersed in a triethanolamine, o-methoxyphenol, sodium metabisulfite solution. The range of the method is approximately 20 to 700 $\mu\text{g}/\text{m}^3$.

The method was evaluated to determine its usefulness. This involved a review of the procedure, as developed, to judge the adequacy of the development work and ruggedness testing, as described by Youden.

The method was shown to be free from interferences such as: NO , SO_2 , O_3 , CO , and NH_3 and possesses a constant-high collection efficiency, 93%. The ruggedness test showed the method to be insensitive to normal variations in: time between sample collection and analysis, storage conditions after sample collection, flow rate, CO_2 concentration, sampling time, and orifice size. The time interval between the addition of the diazonium salt forming reagent and the diazonium salt coupling reagent is critical and must be carefully controlled.

The method appears to be a reliable procedure for the measurement of NO_2 in ambient air.

The method will now be subjected to a collaborative test to determine its repeatability, reproducibility, and bias.

SECTION I

INTRODUCTION

Since the promulgation in the Federal Register of the reference method for the determination of nitrogen dioxide in the atmosphere,⁽¹⁾ the inadequacies of the method have been brought forth. Researchers within⁽²⁾ and outside⁽³⁾ of EPA found a variable collection efficiency and a positive nitric oxide interference. After further evaluation, the Administrator on June 14, 1972, stated that the reference method for measuring nitrogen dioxide was suspected of being unreliable and was being withdrawn. Recently,⁽⁴⁾ EPA has chosen three tentative methods for replacement of the original reference method:

- a. a manual arsenite-alkali method.
- b. a continuous Saltzman procedure.
- c. a continuous chemiluminescence procedure.

The Administrator in his proposal for the consideration and comment on these three methods also asked any interested persons to submit information and comments pertinent to other new methods for NO₂ detection.

Since the task of Methods Standardization Branch (MSB), Quality Assurance and Environmental Monitoring Laboratory (QAEML), is to standardize methods for making air pollution measurements with particular emphasis on the reference methods, we were interested in the three proposed methods and any new methods.

A new manual method⁽⁵⁾ for the detection and analysis of NO_2 in ambient air was chosen to be included in the MSB laboratory evaluation program due to its reported high collection efficiency (93%) and freedom from suspected interferences. The method is based on the sampling of NO_2 from ambient air using an aqueous solution of triethanolamine containing small amounts of o-methoxyphenol and sodium metabisulfite, with subsequent measurement of the nitrite ion by a conventional diazotization-coupling reaction. The work reported here describes an evaluation of this method.

SECTION II

EXPERIMENTAL

The specific reagents and procedures used in this evaluation were exactly the same as those specified in the method write-up. (See Appendix A)

A. Generation of NO₂ Test Atmospheres

The various test atmospheres in this evaluation were generated using a permeation device and known amounts of clean dilution air. This procedure has been described by O'Keeffe and Ortman⁽⁶⁾ and Scaringelli et al.^(7,8)

An FEP-Teflon-sleeve, glass reservoir permeation device developed by the National Bureau of Standards (NBS) and the Environmental Protection Agency (EPA) was used as the source of NO₂.⁽⁹⁾ This device (No. 7-35) was calibrated gravimetrically⁽¹⁰⁾ and had a permeation rate of 1.188 ± 0.002 $\mu\text{g NO}_2/\text{min}$ (95% C.I.) at $25.0 \pm 0.1^\circ\text{C}$. The rate constancy of this device was well established as shown by the data in Figure 1.

The temperature of the device was controlled by a water-jacketed condenser, which was maintained at $25.0 \pm 0.1^\circ\text{C}$ by a Forma Temp., Jr. constant temperature bath. The NO₂ was flushed from the condenser with dry nitrogen at approximately 50 cc/min. The flushing nitrogen was obtained from an A-type cylinder of extra dry grade nitrogen. This was passed through a column of molecular sieve (6-16 mesh, type 4-A) and indicating Drierite.

The dilution air was compressed house air which was passed through an air filter (Wilkerson Corporation Model No. 1237-2F) to remove dirt particles and aerosols, indicating silica gel (6-16 mesh) and activated charcoal (6-16 mesh).

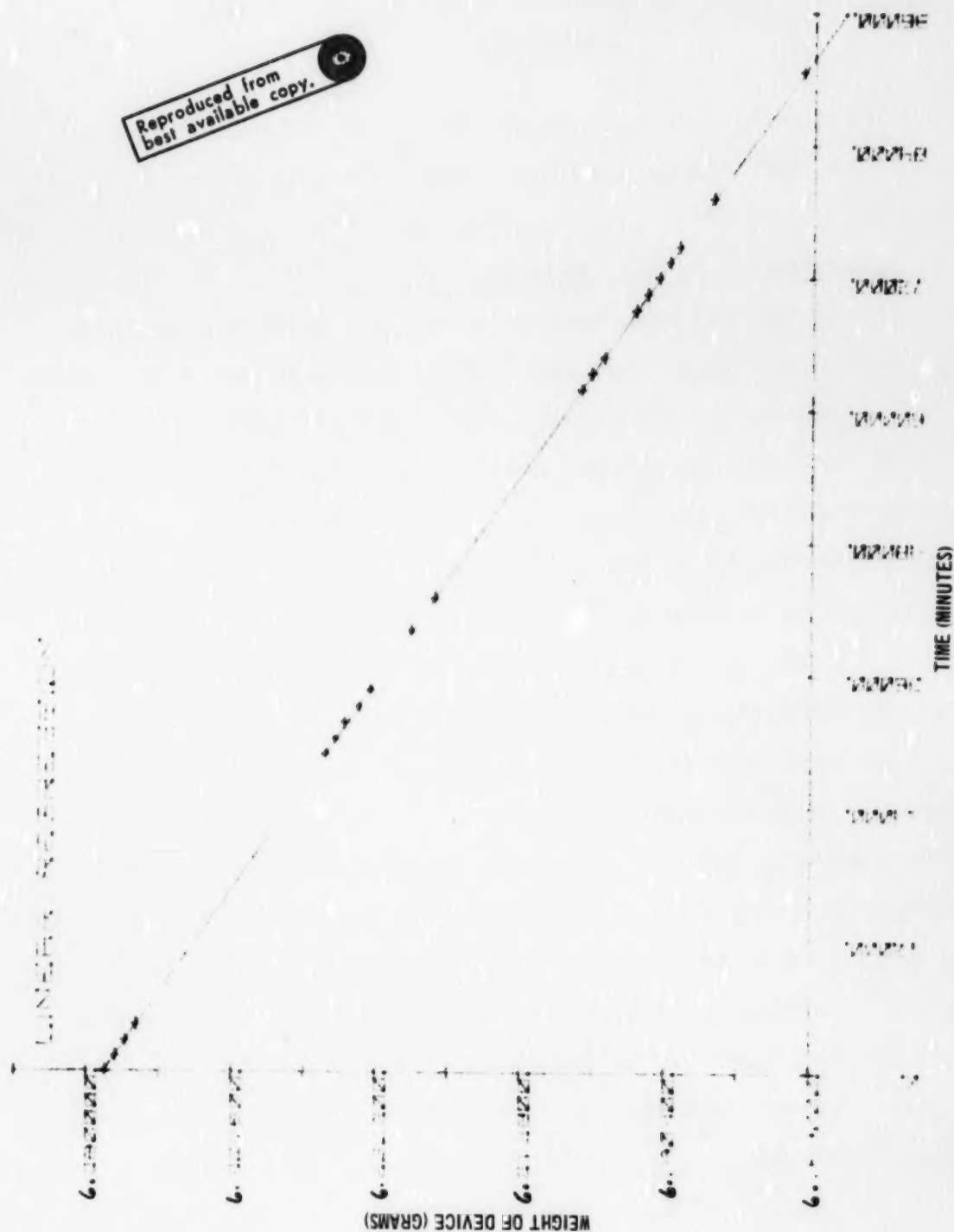


Figure 1. NO_2 permeation rate for device 7-35. (May 1 - July 3, 1973 @ $25^\circ \pm 0.1^\circ\text{C}$ 64 days)

A blank, consisting of a 24-hour sampling of dilution air plus flushing nitrogen with no permeation device in the system, showed a NO_2 concentration of less than $2 \mu\text{g NO}_2/\text{m}^3$. Thus, the generation system was free from interferences.

B. Sampling System

Five sampling trains were placed in parallel to a common inlet glass manifold. In this way each recorded effect was an average of five determinations. Each sampling train sampled the test atmosphere at approximately 200 cc/min. by using a 27-gauge, stainless-steel hypodermic needle as the critical orifice. A Gast Model 0211 oil-less vacuum pump was used to maintain a pressure drop across each orifice of approximately 0.7 of an atmosphere. The time of sampling was either 20 or 24 hours.

The total flow through the sampling trains was measured and compared to the summation of the individual train flows. This is a check to detect any leaks in the system. Differences of greater than 10% constituted a basis for rejecting a sample.

C. Flow Measurement

All flow measurements were made using a wet test meter (1 L/rev , 10 L/rev) or a bubbler flow meter. All flow measurements were an average of an initial and a final flow. The total dilution air flow never varied more than one percent in any 24-hour sampling period, based on differences in initial and final readings.

D. Analysis

Using a Beckman Model B spectrophotometer at a wavelength of 550 nm with one centimeter cells, the absorbance of each sample was read against a blank.

following the analytical procedure of the method.

E. Concentration of Carbon Dioxide

The carbon dioxide used in these experiments was obtained from two different A-type cylinders with concentrations of 1060 ppm CO_2 in nitrogen and 99.9% CO_2 . Both cylinders were previously checked for NO and NO_2 by a $\text{NO-NO}_2\text{-NO}_x$ chemiluminescent monitor. None was detected.

F. Restricted Orifice Bubbler

The restricted-orifice bubblers specified in the method were obtained from a local glassblower. Only those orifices meeting the method specifications were used.

SECTION III

RESULTS AND DISCUSSION

A. Procedure Review

The procedure used by MSB in standardizing a method involves a critical investigation of the method in three phases. Phase one is a procedure review. This consists of evaluating the method on its potential for making meaningful measurements, based on the write-up, obtained from, and conversations with, the developers.

Phase two consists of a laboratory evaluation to determine how well the method measures the pollutant of interest when challenged by variations in the procedure which might occur in the field use of the method.

If a method proves to be reliable after MSB's evaluation, it can be subjected to a collaborative test designed to determine its precision (repeatability and reproducibility) and its accuracy (bias). The collaborative test is the final phase of the standardization process and is a measure of the performance of the method in actual use.

Following this procedure, a copy of the TGS-ANSA method was obtained from the developers, the Laboratory Methods Research Section of the Chemistry and Physics Laboratory, for procedure review.

The method write-up specifies bubbling ambient air through a solution containing triethanolamine, o-methoxyphenol, and sodium metabisulfite. This converts NO_2 gas to nitrite ion (NO_2^-), which is then assayed by diazotization and coupling using sulfanilamide and the ammonium salt of 8-anilino-1-naphthalene-sulfonic acid (ANSA). The absorbance of the pink-purple dye is read at 550 nm and the values converted to nitrite ion concentration by use of a calibration curve.

The function of the triethanolamine (TEA) is to provide a basic collecting media. When used by itself, the (TEA) produces an overall collection efficiency of 85%⁽¹¹⁾ with a fritted glass bubbler. The o-methoxyphenol(guaiacol) increases the collection efficiency.⁽¹²⁾ It is also relatively stable, among phenoxides, in alkaline solution. This reagent when added to the (TEA) improves the overall collection efficiency to 93% using a restricted glass orifice.

The developers found that the triethanolamine and guaiacol system (TG) showed reduced efficiency with age and developed a yellow color. It was suspected that the guaiacol was forming quinones with age which affected the efficiency and produced the yellow color. A free radical inhibitor, sodium metabisulfite, was added to reduce the formation of quinones. With the addition of the sulfite ion, it was noted that the dye formed in the sulfanilamide, n-(1-naphthyl)ethylene-diamine dihydrochloride reaction was being bleached; therefore, new diazotization-coupling reagents had to be found.

Knowing from previous work that ANSA would be stable under these conditions, the developers tried this coupling reagent with various diazonium salt precursors; sulfanilamide in HCl proved to give the most reproducible results. A novel feature of this analytical system is the high range of analysis, up to 4.0 $\mu\text{g/ml}$ of NO_2^- , possible without sample dilution.

The developers also showed data that the TGS-ANSA method was both constant in overall efficiency (93%) from 20 to 700 $\mu\text{g/m}^3$ and free from a

number of probable interferences such as: NO, SO₂, O₃, NH₃, CO, CH₂O, and phenol.

With these and other facts brought forth by the developers, the TGS-ANSA method was judged to be sufficiently well developed to proceed directly to the laboratory evaluation without further development. A copy of the write-up, developed as a result of this procedure review, is given in Appendix A. It differs from the original only in minor technical modifications and editorial changes.

B. Ruggedness Testing

1. Design

Once a method is deemed ready for laboratory testing (Phase II), it is desirable to subject the method to slight variations in important parameters as would be expected to occur in normal usage. This can be accomplished by ruggedness testing. This is done by studying selected variables at two levels; the nominal level stated in the method write-up, and a challenging level. A procedure has been developed by Youden⁽¹³⁾ to determine the effect of a variable by comparing the results obtained at the two levels. To accomplish this, seven^(a) variables are chosen for study and their nominal levels designated A to G. A challenging level is then selected and denoted by the corresponding lower case letter, a to g. A series of eight

(a) Schemes for examining the effect of a larger or smaller number of variables are available.⁽¹⁴⁾

experiments are then conducted using various combinations of either nominal or challenging values for each variable. The format for these experiments is shown in Table 1.

Each of the eight experiments produces a result, denoted as s, t, u, v, w, x, y, and z. Examination of the format in Table 1 reveals that by summing the group of experiment results in which a given nominal value was involved and subtracting from it the sum of the group of results in which the corresponding challenging value was involved, the effect of all other variables are canceled. If the grouped results are divided by the number in each group, the above subtraction will yield the average effect or difference between the nominal and challenging conditions.

For example, the average effect of variable E is calculated using:

$$E-e = \frac{s + u + x + z}{4} - \frac{t + v + w + y}{4}$$

A complete set of equations for calculating the effect of A-a, B-a, etc. are given in Appendix B.

It should be noted that the results of the ruggedness test will not completely describe the effect of varying a given parameter. The results only show the effect of the range of variation used in the experiment. If the effect is shown to be significant, further experimentation will be needed to define the exact relationship.

Thus, the ruggedness test design permits the screening of the effect of seven variables with only eight experiments. Without this design, it would require 2^7 or 128 experiments to investigate the effect of seven variables at two levels.

Table 1. RUGGEDNESS TEST FORMAT

EXPERIMENTS							
1	2	3	4	5	6	7	8
A	A	A	A	a	a	a	a
B	B	b	b	B	B	b	b
C	c	C	c	C	c	C	c
D	D	d	d	d	d	D	D
E	e	E	e	e	E	e	E
F	f	f	F	F	f	f	F
G	g	g	G	g	G	G	g
OBSERVED RESULTS							
s	t	u	v	w	x	y	z

2. Selection of Variables

In evaluating any method there are, of course, many variables that could be studied, but the following were deemed most important:

a. NO_2 concentration

$$A = 70 \text{ } \mu\text{g NO}_2/\text{m}^3$$

$$a = 600 \text{ } \mu\text{g NO}_2/\text{m}^3$$

The effect of various concentrations of NO_2 on the method had been previously evaluated in the determination of collection efficiency. However, the effect of other variables in association with the NO_2 concentration was not known. Therefore, NO_2 concentrations of 70 and 600 $\mu\text{gNO}_2/\text{m}^3$ were chosen to cover the range of the method.

b. Flow rate

$$B = 200 \text{ cm}^3/\text{min.}$$

$$b = 350 \text{ cm}^3/\text{min.}$$

The method requires a flow rate of 180 to 220 $\text{cm}^3/\text{min.}$ Since the collection efficiency of a method can be affected by the rate of delivery of the sample to the absorbing solution, it was decided to examine the effect of flow rates. Accordingly, nominal and challenging flows of 180 to 220 and 310 to 340 $\text{cm}^3/\text{min.}$ respectively were selected.

c. CO_2 concentration

$$C = \text{ambient}$$

$$c = \text{ambient} + 250 \text{ ppm}$$

CO_2 absorbed in the absorbing solution will produce a change in pH which can, in turn, affect the collection efficiency. To test the significance of this effect, 250 ppm of CO_2 was added to the ambient (nominal)

level of CO₂.

d. Orifice size

D = 0.3 to 0.4 mm

d = 0.6 mm

Orifice size can affect collection efficiency by controlling the surface area of the bubbles produced in the solution. A test of the effect of an orifice diameter outside the prescribed 0.3 to 0.4 mm was made by using 0.6 mm for the challenging value.

e. Time between collection and analysis

E = 2-4 days

e = 2 weeks $\pm$ 2 days

This parameter was chosen because of the possibility of color formation in the absorbing solution if the effectiveness of the free radical inhibitor was reduced on aging of the collected samples. Samples were stored on the laboratory bench and analyzed at the indicated times.

f. Storage conditions after sampling

F = in the dark

f = on the laboratory bench

The use of a manual method, in practice, usually involves shipping the collected samples to a central laboratory for analysis. During shipment, of course, the samples are in the dark. Subsequent exposure to light prior to analysis could accelerate color formation if the free radical inhibitor was not effective. Accordingly, samples were stored in the dark and on the laboratory bench for the times called for in the ruggedness test

format, 2-4 days or 2 weeks.

g. Sampling time

G = 24-hours

g = 20-hours

When a method specifies taking a 24-hour sample, sampling periods of less than 24 hours sometimes occur when the 24-hour period terminates at the end of the working day. Since the effect of this variation in sampling time had not been studied, it was included as a variable. The challenging level was set at four hours less than the nominal value.

3. Conducting the Ruggedness Test

The parameters chosen for the ruggedness test were incorporated into the format shown in Table 1 and the experiments conducted in random order (2, 3, 5, 7, 4, 1, 8, 6). The individual and average results for each experiment are given in Appendix C. It should be noted that the results are expressed in percent. This was calculated by dividing the concentration found by the concentration of NO_2 generated. This normalization of the results was necessary before the effect of the different parameters could be determined because, the method is obviously sensitive to NO_2 concentration.

The results in Appendix C were substituted into the equations of Appendix B and the effect of each parameter was calculated. The net results are shown, ranked in order of decreasing absolute magnitude, in Table 2.

Table 2. SUMMARY OF RUGGEDNESS TEST RESULTS

<u>Variable</u>	<u>Levels</u>	<u>Difference, %</u>
Orifice size	D = 0.3 - 0.4 mm d = 0.6 mm	-7.4
NO ₂ concentration	A = 70 $\mu\text{g NO}_2/\text{m}^3$ a = 600 $\mu\text{g NO}_2/\text{m}^3$	-2.6
Time between collection and analysis	E = 2-4 days e = 2 weeks	2.5
Flow rate	B = 200 cc/min b = 350 cc/min	2.0
Storage conditions after sampling	F = in dark f = on bench	1.8
CO ₂ concentration	C = ambient c = ambient + 250 ppm	1.6
Time of sampling	G = 24 hours g = 20 hours	1.0

4. Results

Inspection of the data shows that six of the seven variables examined (NO_2 concentration, time between collection and analysis, flow rate, storage conditions after sampling, CO_2 concentration, and sampling time) gave differences in response of only 1.0 to 2.6%. Since the standard deviation for the collection efficiency of the method (see section 4.1.1, Appendix A) is 2%, these differences do not appear significant. Changing the orifice size from its nominal value of 0.3 to 0.4 mm to 0.6 mm, however, produced a difference of -7.4%. Numerically, this appears to be significant; however, the fact that the value is negative indicates that increasing the orifice size produced an increase in the method response (collection efficiency). An increase in orifice size should, if anything, reduce the collection efficiency because the total surface area of the air bubbles is being reduced. Thus, this result may be anomalous. No further experimentation is planned to investigate this point.

Subsequent to this work, the TGS-ANSA method was used by the Analytical Chemistry Branch of QAEML to analyze a large number of collected samples. During this work, it was found that the time interval between formation of the diazonium salt of sulfanilamide and addition of the ANSA coupling reagent, in the analytical scheme, was critical. This led us to examine the effect of this variable. The experiments involved used intervals of 2, 4, 8, 16, 32 and 64 minutes and measured the absorbance produced. The results showed that time intervals up to eight minutes had no effect on absorbance; at the 16 minute interval the absorbance was significantly decreased.

Based on these results and a report on the use of the method, issued by ACB, a revised-improved write-up was generated. A copy is included as Appendix D. Attention is directed to the caution statements in Sections 6.2.9 and 7.2.

SECTION IV

CONCLUSIONS

The TGS-ANSA method is insensitive to normal variations in: time between sample collection and analysis, flow rate, storage conditions after sample collection, CO_2 concentration, sampling time, and (most likely) orifice size.

No interferences have been detected in the method.

Thus, the TGS-ANSA method appears to be a reliable procedure for the measurement of NO_2 in ambient air, provided the revised version of the method is followed.

SECTION V

FUTURE WORK

This will involve additional distribution of the revised method write-up to interested laboratories and soliciting the results of their experience in using the method. This information should aid in further refinement of the method.

The revised method will also be subjected to a collaborative test (tentatively scheduled for May, 1974) to determine its repeatability, reproducibility and bias.

MSB will carry out experiments, as time becomes available, to optimize the time interval between formation of the diazonium salt and addition of the coupling reagent (Section 7.2 - Appendix D); specifications on reagent stability will also be optimized.

SECTION VI

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SECTION VII

APPENDICES

- A. "Tentative Method for Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA Procedure)."
- B. Equations for Calculating Ruggedness Test Results.
- C. Data from Ruggedness Test.
- D. Revised, February 1974, method write-up.

Appendix A

ENVIRONMENTAL PROTECTION AGENCY
METHODS STANDARDIZATION BRANCH
QUALITY ASSURANCE AND ENVIRONMENTAL MONITORING LABORATORY
NATIONAL ENVIRONMENTAL RESEARCH CENTER
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

NOVEMBER 1973

TENTATIVE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE
IN THE ATMOSPHERE (TGS-ANSA)^a

^aA tentative method is one which has been carefully drafted from available experimental information, reviewed editorially within the Methods Standardization Branch and has undergone extensive laboratory evaluation. The method is still under investigation and therefore is subject to revision.

1. Principle and Applicability

1.1 Nitrogen dioxide is collected by bubbling air through a solution of triethanolamine, o-methoxyphenol and sodium metabisulfite.¹ The nitrite ion produced during sampling is determined colormetrically by reacting the exposed absorbing reagent with sulfanilamide and 8-anilino-1-naphthalenesulfonic acid.

1.2 The method is applicable to collections of 24-hour samples in the field and subsequent analysis in the laboratory.

2. Range and Sensitivity

2.1 The range of the analysis is 0.025 to 4.0 $\mu\text{g NO}_2^-/\text{ml}$. Beer's law is obeyed throughout this range. With 50 ml of absorbing reagent and a sampling rate of 200 cm^3/min for 24-hours, the range of the method is 20 to 700 $\mu\text{g}/\text{m}^3$ nitrogen dioxide.

2.2 A concentration of 0.025 $\mu\text{g NO}_2^-/\text{ml}$ will produce an absorbance of approximately 0.013 using 1 cm cells.

3. Interferences

3.1 At a nitrogen dioxide concentration of 100 $\mu\text{g}/\text{m}^3$ the following pollutants, at the levels indicated, do not interfere: ammonia, 205 $\mu\text{g}/\text{m}^3$; carbon monoxide, 154,000 $\mu\text{g}/\text{m}^3$; formaldehyde, 750 $\mu\text{g}/\text{m}^3$; nitric oxide, 734 $\mu\text{g}/\text{m}^3$; phenol, 150 $\mu\text{g}/\text{m}^3$; ozone, 400 $\mu\text{g}/\text{m}^3$ and sulfur dioxide, 439 $\mu\text{g}/\text{m}^3$.

3.2 A temperature of 40°C during collection of sample had no effect on recovery.

4. Precision and Accuracy

4.1 Precision and Accuracy

4.1.1 On making measurements from standard nitrogen dioxide atmospheres, prepared by using permeation devices, a relative standard deviation of 2% and a collection efficiency of 93% were determined throughout the range of the method.

4.2 Stability

4.2.1 The absorbing reagent is stable for 3 weeks before sampling and the collected samples are stable for 3 weeks after sampling.

5. Apparatus

5.1 Sampling. A diagram of a suggested sampling apparatus is shown in Figure A-1.

5.1.1 Probe. Teflon, polypropylene, or glass tube with a polypropylene or glass funnel at the end.

5.1.2 Absorption tube. Polypropylene tubes 164 x 32 mm. equipped with polypropylene two-port closures. Rubber stoppers cause high and varying blank values and should not be used. A glass tube restricted orifice is used to disperse the gas. The tube, approximately 8 mm O.D.-6 mm. I.D., should be 152 mm long with the end drawn out to 0.3-0.6 mm. I.D.^(a) The tube should be positioned so as to allow a clearance of 6 mm from the bottom of the absorber.

5.1.3 Moisture trap. Polypropylene tube equipped with a two port closure. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with glass wool to prevent moisture entrainment.

(a) This specification was modified from the original 0.3 to 0.4 mm. to reflect the results of the ruggedness test.

5.1.4 Membrane Filter, 0.8-2.0 microns porosity.

5.1.5 Flow Control Device. Any device capable of maintaining a constant flow through the sampling solution between 180-220 cm³/min. A typical flow control device is a 27 gauge hypodermic needle,² three-eighths inch long. (Most 27 gauge needles will give flow rates in this range.) The device used should be protected from particulate matter. A membrane filter is suggested. Change filter after collecting 10 samples.

5.1.6 Air Pump. Capable of maintaining a pressure differential of at least 0.6-0.7 of an atmosphere across the flow control device. This value includes the minimum useful differential, 0.53⁽²⁾ atmospheres, plus a safety factor to allow for variations in atmospheric pressure.

5.1.7 Calibration Equipment. Flowmeter for measuring airflows up to 275 cm³/min. within $\pm 2\%$, stopwatch, and a precision wet test meter (1 liter/revolution).

5.2 Analysis

5.2.1 Volumetric Flasks. One each 200, 250, 1000 ml; 6 each 100 ml.

5.2.2 Pipets, volumetric. Two each 0.5; one each 3, 4, 5, 6, 10 ml.

5.2.3 Pipets serological, graduated in 1/10 ml divisions. One each 1, 5 ml.

5.2.4 Test Tubes. Each approximately 20 x 150 mm.

5.2.5 Spectrophotometer. Capable of measuring absorbance at 550 nm.

5.2.6 Graduated cylinder. One each 50 ml.

6. Reagents

6.1. Sampling

6.1.1 Triethanolamine [$\text{N}(\text{C}_2\text{H}_4\text{OH})_3$]. Reagent grade.

6.1.2 o-Methoxyphenol ($\text{o-CH}_3\text{OC}_6\text{H}_4\text{OH}$). Also known by its trivial name, guaiacol. Reagent grade. Melting point $27-28^\circ\text{C}$.

6.1.3 Sodium Metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$). ACS reagent grade.

6.1.4 Absorbing Reagent - Dissolve 20g of triethanolamine, 0.5g of o-methoxyphenol, and 0.250g of sodium metabisulfite consecutively in 500 ml of distilled water. Dilute to one liter with distilled water. Mix thoroughly. The solution should be colorless. This solution is stable for four weeks, if kept refrigerated.

6.2 Analysis

6.2.1 Hydrogen Peroxide (H_2O_2). ACS reagent grade, 30%.

6.2.2 Sulfanilamide [$4-(\text{H}_2\text{N})\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$]. Melting point $165-167^\circ\text{C}$.

6.2.3 8-Anilino-1-naphthalenesulfonic acid ammonium salt (ANSA) ($8-\text{C}_6\text{H}_5\text{NH}-1-\text{C}_{10}\text{H}_6\text{SO}_3^-\text{NH}_4^+$).

6.2.4 Sodium Nitrite. [NaNO_2]. ACS reagent grade. Assay of 97% NaNO_2 or greater.

6.2.5 Methanol, absolute [CH_3OH]. ACS reagent grade (Acetone free).

6.2.6 Hydrochloric acid, [HCl]. Concentrated. ACS reagent grade.

6.2.7 Hydrogen Peroxide Solution. Dilute 0.2 ml of 30% hydrogen peroxide to 250 ml with distilled water. This solution can be used for a month if protected from light and refrigerated.

6.2.8 Sulfanilamide Solution (2.0% in 4N HCl). Dissolve 2.0 g of sulfanilamide in 33 ml of concentrated HCl and dilute to 100 ml with distilled water. Mix. This solution can be used for a month, if refrigerated.

6.2.9 ANSA Solution. Dissolve 0.1g ANSA in 50 ml absolute methanol. Dilute to 100 ml with absolute methanol. Mix. Keep stoppered when not in use. This solution can be used for a month, if refrigerated.

6.2.10 Standard Nitrite Solution. Dissolve sufficient desiccated sodium nitrite and dilute with distilled water to 1000 ml so a solution containing $1000 \mu\text{gNO}_2^-/\text{ml}$ is obtained. The amount of NaNO_2 to use is calculated as follows:

$$G = \frac{1.500}{A} \times 100$$

where

G = Amount of NaNO_2 , grams.

1.500 = Gravimetric factor in converting NO_2 into NaNO_2

A = Assay, percent

7. Procedures

7.1 Sampling. Assemble the sampling apparatus, as shown in Figure A-1. Components upstream from the absorption tube may be connected, where required, with teflon or polypropylene tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with tygon, teflon or polypropylene. Add exactly 50 ml of absorbing reagent to the calibrated absorption tube

(8.1.3). Disconnect funnel, insert calibrated flowmeter (8.1.1) into the end of the probe and measure flow before sampling. Denote as F_1 . If flow rate before sampling is not between 180-220 cm^3/min replace the flow controlling device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range. Sample for 24-hours and measure the flow after sampling by again inserting a calibrated flowmeter into the probe, after removing the funnel. Denote as F_2 .

7.2 Analysis. Replace any water lost by evaporation during sampling by adding distilled water up to the calibrated mark on the absorption tube. Mix well. Pipet 5 ml of the collected sample into a test tube, add 0.5 ml of the peroxide solution and mix vigorously for approximately 15 seconds. Add 2.7 ml of sulfanilamide solution and mix vigorously for about 30 seconds. Then pipet 3 ml of the ANSA solution, mix vigorously for about 30 seconds. Mechanical mixing is recommended. Prepare a blank in the same manner using 5 ml of unexposed absorbing solution. Determine absorbance at 550 nm against the blank solution using 1 cm cells. The color is stable for 30 minutes. Read $\mu\text{g NO}_2^-/\text{ml}$ from the calibration curve (Section 8.2).

7.3 Spectrophotometer cells must be rinsed thoroughly with distilled water, acetone, and dried, otherwise a film will build up on the cell walls.

8. Calibration and Efficiencies

8.1 Sampling

8.1.1 Calibration of Flowmeter. (See Figure A-2.) Using a wet test meter and a stopwatch, determine the rates of air flow (cm^3/min) through the flow-

meter at a minimum of four different ball positions. Plot ball position versus flow rate.

8.1.2 Flow Control Device. The flow control device results in a constant rate of air flow through the absorbing solution and is determined in 7.1.

8.1.3 Calibration of Absorption Tube. Calibrate the polypropylene absorption tube (Section 5.1.2) by first pipeting in 50 ml of water or absorbing reagent. Scribe the level of the meniscus with a sharp object, go over the area with a felt-tip marking pen, and rub off the excess.

8.2 Calibration Curve. Dilute 5.0 ml of the 1000 $\mu\text{g NO}_2^-/\text{ml}$ solution to 200 ml with absorbing reagent. This solution contains 25 $\mu\text{g NO}_2^-/\text{ml}$. Pipet 0.5, 4, 10, 16 ml of the 25 $\mu\text{g NO}_2^-/\text{ml}$ solution into 100 ml volumetric flasks and dilute to the mark with absorbing reagent. These solutions contain 0.125, 1.0, 2.5, 4.0 $\mu\text{g NO}_2^-/\text{ml}$, respectively. Run standards as instructed in 7.2. Plot absorbance vs $\mu\text{g NO}_2^-/\text{ml}$. A straight line should be obtained.

8.3 Efficiencies. An overall average efficiency of 93% was obtained from test atmospheres having a nitrogen dioxide concentration of 20 to 700 $\mu\text{g}/\text{m}^3$.

9. Calculation

9.1 Sampling

9.1.1 Calculate volume of air sampled.

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6}$$

- V = Volume of air sampled, m^3 .
 F_1 = Measured flow rate before sampling, cm^3/min .
 F_2 = Measured flow rate after sampling, cm^3/min .
 T = Time of sampling, min.
 10^{-6} = Conversion of cm^3 to m^3 .

9.1.2 Uncorrected Volume. The volume of air sampled is not corrected to S.T.P., because of the uncertainty associated with 24-hour average temperature and pressure values.

9.2 Calculate the concentration of nitrogen dioxide as $\mu g NO_2/m^3$.

$$\mu g NO_2/m^3 = \frac{(\mu g NO_2/ml) \times 50}{V \times (0.93)^a}$$

50 = Volume of absorbing reagent used in sampling, ml.

V = Volume of air sampled, m^3 .

0.93 = Overall efficiency of method.

9.2.1 If desired, concentration of nitrogen dioxide may be calculated as ppm NO_2 .

$$ppm = (\mu g NO_2/m^3) \times 5.32 \times 10^{-4}$$

10. References

- Mulik, J. D., Fuerst, R. G., Meeker, J. R., Guyer, M., Sawicki, E.
 "A Twenty-Four Hour Method for the Collection and Manual Colorimetric Analysis of Nitrogen Dioxide. Presented at the 165th ACS National Meeting in Dallas, Texas, April 8-13, 1973.
- Lodge, J. P., Jr., Pate, J. B., Ammons, B. E., Swanson, G. A. "The Use of Hypodermic Needles as Critical Orifices in Air Sampling."
 J.A.P.C.A. 16, 197-200 (1966).

^a The correction for collection efficiency was added to the method after the ruggedness test.

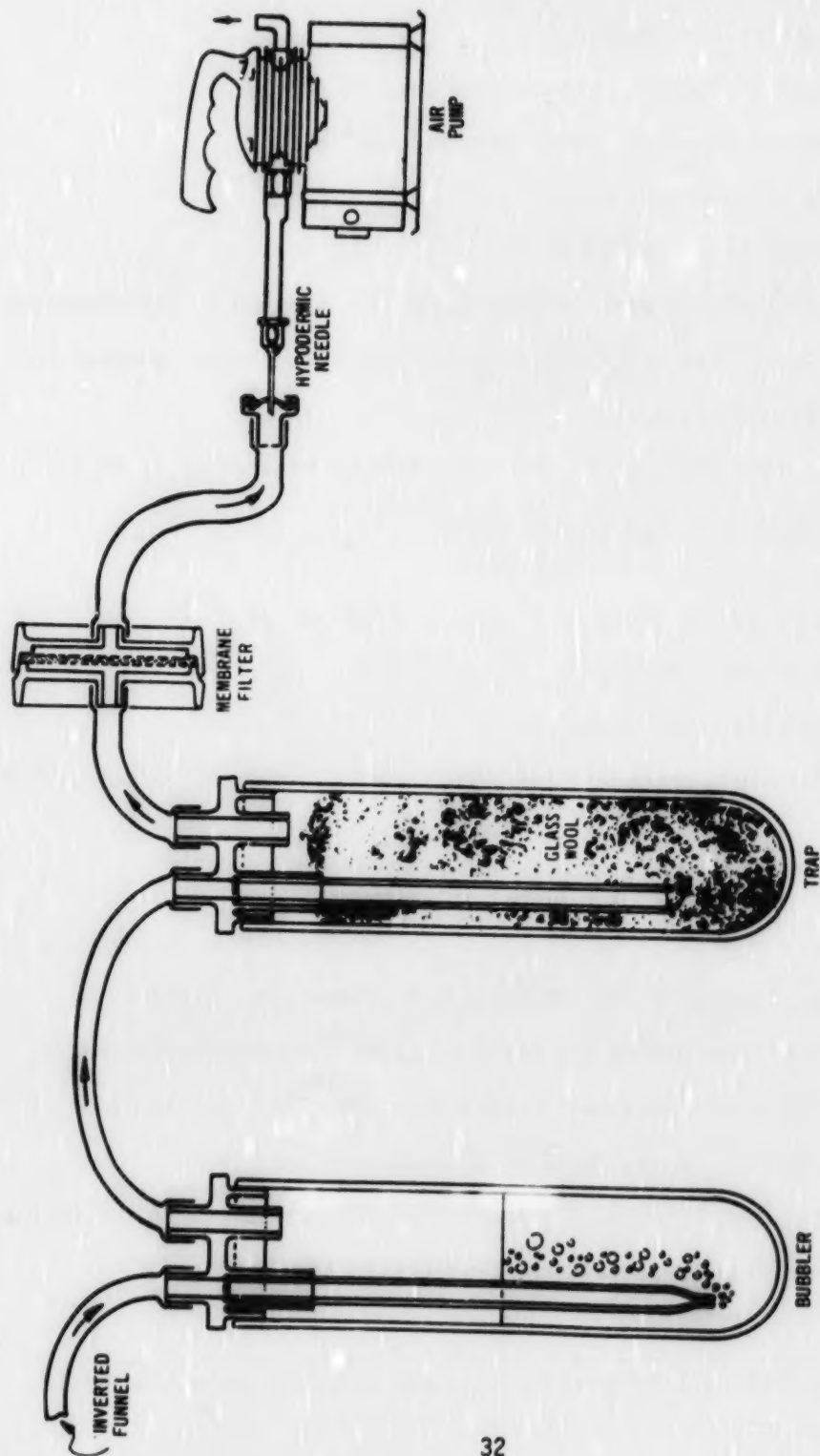


Figure A-1. Sampling train.

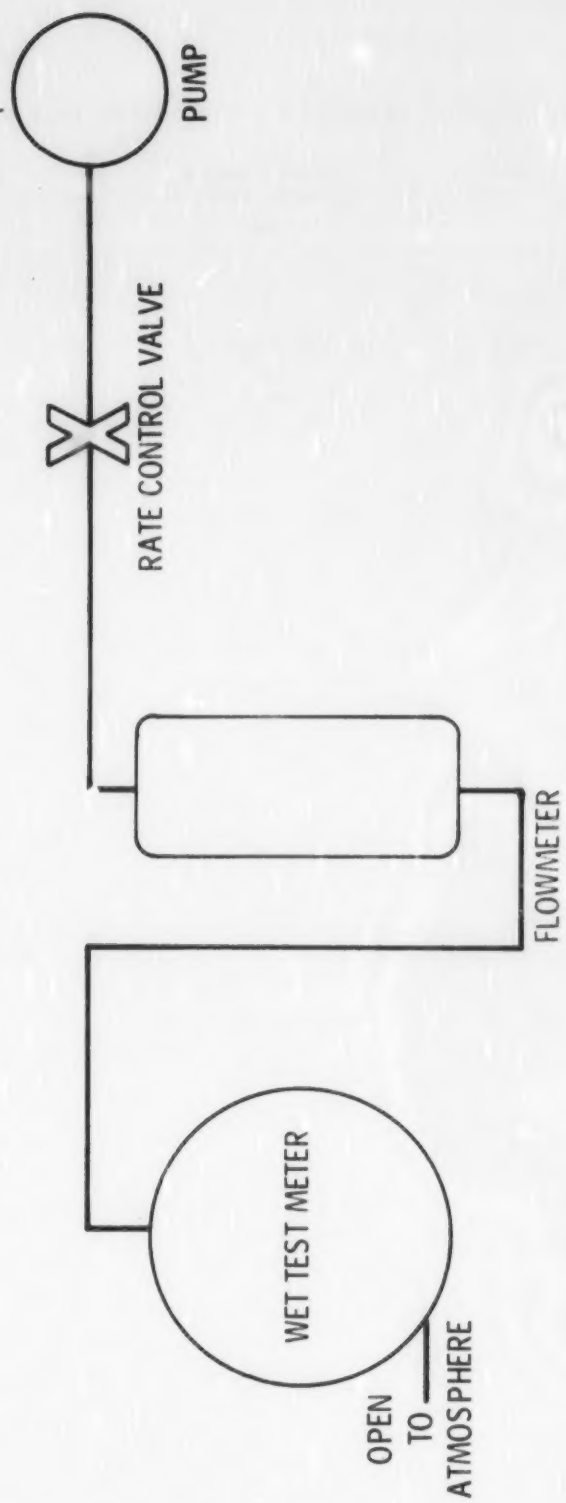


Figure A-2. Flowmeter.

Appendix B. Equations for Calculating Ruggedness Test Results.

$$A-a = \frac{S+t+u+v}{4} - \frac{w+x+y+z}{4}$$

$$B-b = \frac{S+t+w+x}{4} - \frac{u+v+y+z}{4}$$

$$C-c = \frac{S+u+w+y}{4} - \frac{t+v+x+z}{4}$$

$$D-d = \frac{S+t+y+z}{4} - \frac{u+v+w+x}{4}$$

$$E-e = \frac{S+u+x+z}{4} - \frac{t+v+w+y}{4}$$

$$F-f = \frac{S+v+w+z}{4} - \frac{t+u+x+y}{4}$$

$$G-g = \frac{S+v+x+y}{4} - \frac{t+u+w+z}{4}$$

Appendix C. Data from Ruggedness Test.

Expt. No.	Result	NO ₂ ⁻ $\mu\text{g}/\text{m}^3$ Generated	Found	$\mu\text{g NO}_2^-/\text{ml}$ Found ²	Response, %	Mean Response, %
1	s	76.5	69.9	0.422	91.4	92.9
		76.4	68.7	0.414	89.9	
		76.4	69.6	0.433	91.1	
		76.4	73.6	0.443	96.3	
		76.5	73.4	0.443	95.9	
2	t	78.4	72.1	0.169	92.0	86.0
		78.3	62.5	0.142	79.8	
		78.2	67.9	0.157	86.8	
		78.5	67.9	0.152	86.5	
		78.3	66.5	0.155	84.9	
3	u	77.1	73.1	0.615	94.8	95.4
		77.0	72.6	0.615	94.3	
		77.1	72.9	0.596	94.6	
		77.1	74.3	0.615	96.4	
		77.2	74.8	0.605	96.9	
4	v	76.7	68.5	0.690	89.3	94.1
		76.7	68.7	0.704	89.6	
		76.8	66.7	0.651	86.8	
		76.8	86.1	0.857	112.1	
		77.5	71.7	0.681	92.5	
5	w	594.7	591.0	3.038	99.4	99.4
		594.6	587.8	2.951	98.9	
		592.8	570.0	2.953	96.2	
		593.7	606.9	3.095	102.2	
		593.7	595.6	3.038	100.3	
6	x	591.2	580.5	3.413	98.2	99.4
		591.6	578.3	3.481	97.8	
		592.5	592.2	3.577	99.9	
		592.2	590.9	3.604	99.8	
		591.8	599.8	3.575	101.4	
7	y	590.4	552.2	5.301	93.5	89.1
		590.6	490.3	4.776	83.0	
		591.0	505.7	4.733	85.6	
		590.9	546.2	5.254	92.4	
		590.7	537.3	5.094	91.0	
8	z	592.1	557.8	4.351	94.2	90.9
		592.5	503.9	4.001	85.0	
		591.8	536.1	4.171	90.6	
		592.1	545.6	4.452	92.1	
		592.1	547.1	4.399	92.4	

APPENDIX D

ENVIRONMENTAL PROTECTION AGENCY
METHODS STANDARDIZATION BRANCH
QUALITY ASSURANCE AND ENVIRONMENTAL MONITORING LABORATORY
NATIONAL ENVIRONMENTAL RESEARCH CENTER
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

FEBRUARY 1974

TENTATIVE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE
IN THE ATMOSPHERE (TGS-ANSA)^a

^aA tentative method is one which has been carefully drafted from available experimental information, reviewed editorially within the Methods Standardization Branch and has undergone extensive laboratory evaluation. The method is still under investigation and therefore is subject to revision.

1. Principle and Applicability

1.1 Nitrogen dioxide is collected by bubbling air through a solution of triethanolamine, o-methoxyphenol and sodium metabisulfite.¹ The nitrite ion produced during sampling is determined colorimetrically by reacting the exposed absorbing reagent with sulfanilamide and 8-anilino-1-naphthalenesulfonic acid, ammonium salt.

1.2 The method is applicable to collections of 24-hour samples in the field and subsequent analysis in the laboratory.

2. Range and Sensitivity

2.1 The range of the analysis is 0.025 to 4.0 $\mu\text{g NO}_2^-/\text{ml}$. Beer's law is obeyed throughout this range. With 50 ml of absorbing reagent and a sampling rate of 200 cm^3/min for 24-hours, the range of the method is 20 to 100 $\mu\text{g}/\text{m}^3$ nitrogen dioxide.

2.2 A concentration of 0.025 $\mu\text{g NO}_2^-/\text{ml}$ will produce an absorbance of approximately 0.025 using 1 cm cells.

3. Interferences

3.1 At a nitrogen dioxide concentration of 100 $\mu\text{g}/\text{m}^3$ the following pollutants, at the levels indicated, do not interfere: ammonia, 205 $\mu\text{g}/\text{m}^3$; carbon monoxide, 154,000 $\mu\text{g}/\text{m}^3$; formaldehyde, 750 $\mu\text{g}/\text{m}^3$; nitric oxide, 734 $\mu\text{g}/\text{m}^3$; phenol, 150 $\mu\text{g}/\text{m}^3$; ozone, 400 $\mu\text{g}/\text{m}^3$ and sulfur dioxide, 439 $\mu\text{g}/\text{m}^3$.

3.2 A temperature of 40°C during collection of sample had no effect on recovery.

4. Precision and Accuracy

4.1 Precision and Accuracy

4.1.1 On making measurements from standard nitrogen dioxide atmospheres, prepared by using permeation devices, a relative standard deviation of 2% and a collection efficiency of 93% were determined throughout the range of the method.

4.2 Stability

4.2.1 The absorbing reagent is stable for 3 weeks before sampling and the collected samples are stable for 3 weeks after sampling.

5. Apparatus

5.1 Sampling. A diagram of a suggested sampling apparatus is shown in Figure D-1.

5.1.1 Probe. Teflon, polypropylene, or glass tube with a polypropylene or glass funnel at the end.

5.1.2 Absorption tube. Polypropylene tubes 164 x 32 mm. equipped with polypropylene two-port closures. Rubber stoppers cause high and varying blank values and should not be used. A glass tube restricted orifice is used to disperse the gas. The tube, approximately 8 mm O.D.-6 mm. I.D., should be 152 mm long with the end drawn out to 0.3-0.6 mm. I.D. The tube should be positioned so as to allow a clearance of 6 mm from the bottom of the absorber.

5.1.3 Moisture trap. Polypropylene tube equipped with a two port closure. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with glass wool to prevent moisture entrainment.

5.1.4 Membrane Filter, 0.8-2.0 microns porosity.

5.1.5 Flow Control Device. Any device capable of maintaining a constant flow through the sampling solution between 180-220 cm^3/min . A typical flow control device is a 27 gauge hypodermic needle,² three-eighths inch long. (Most 27 gauge needles will give flow rates in this range.) The device used should be protected from particulate matter. A membrane filter is suggested. Change filter after collecting 10 samples.

5.1.6 Air Pump. Capable of maintaining a pressure differential of at least 0.6-0.7 of an atmosphere across the flow control device. This value includes the minimum useful differential, 0.53⁽²⁾ atmospheres, plus a safety factor to allow for variations in atmospheric pressure.

5.1.7 Calibration Equipment. Flowmeter for measuring airflows up to 275 cm^3/min . within $\pm 2\%$, stopwatch, and a precision wet test meter (1 liter/revolution).

5.2 Analysis

5.2.1 Volumetric Flasks. Two each 250, 1000 ml; three each 200; 7 each 100 ml; one 500 ml.

5.2.2 Pipets, volumetric. One each, 2, 3, 9, 10, 20 and 50 ml; seven 5-ml

5.2.3 Pipets serological, graduated in 1/10 ml divisions. One each 1, 5 ml.

5.2.4 Test Tubes. Each approximately 20 x 150 mm.

5.2.5 Spectrophotometer. Capable of measuring absorbance at 550 nm.

5.2.6 Graduated cylinder. One each 50 ml.

6. Reagents

6.1 Sampling

6.1.1 Triethanolamine [$N(C_2H_4OH)_3$]. Reagent grade.

6.1.2 o-Methoxyphenol ($o\text{-CH}_3OC_6H_4OH$). Also known by its trivial name, guaiacol. Reagent grade. Melting point 27-28°C. (Caution: Technical grade material will not meet this specification and should not be used).

6.1.3 Sodium Metabisulfite ($Na_2S_2O_5$): ACS reagent grade.

6.1.4 Absorbing Reagent - Dissolve 20g of triethanolamine, 0.5g of o-methoxyphenol, and 0.250g of sodium metabisulfite consecutively in 500 ml of distilled water. Dilute to one liter with distilled water. Mix thoroughly. The solution should be colorless. This solution is stable for three weeks, if kept refrigerated.

6.2 Analysis

6.2.1 Hydrogen Peroxide (H_2O_2). ACS reagent grade, 30%.

6.2.2 Sulfanilamide [$4\text{-(H}_2\text{N)C}_6\text{H}_4\text{SO}_2\text{NH}_2$]. Melting point 165-167°C.

6.2.3 8-Anilino-1-naphthalenesulfonic acid Ammonium salt (ANSA) ($8\text{-C}_6\text{H}_5\text{NH-1-C}_{10}\text{H}_6\text{SO}_3^-\text{NH}_4^+$). Minimum analysis, 98%.

6.2.4 Sodium Nitrite, [$NaNO_2$]. ACS reagent grade. Assay of 97% $NaNO_2$ or greater.

6.2.5 Methanol, absolute [CH_3OH]. ACS reagent grade.

6.2.6 Hydrochloric acid, [HCl]. Concentrated. ACS reagent grade.

6.2.7 Hydrogen Peroxide Solution. Dilute 0.2 ml of 30% hydrogen peroxide to 250 ml with distilled water. This solution can be used for a month if protected from light and refrigerated.

6.2.8 Sulfanilamide Solution (2.0% in 4N HCl). Dissolve 2.0g of sulfanilamide in 33 ml of concentrated HCl and dilute to 100 ml with distilled water. Mix. This solution can be used for two weeks, if refrigerated.

6.2.9 ANSA Solution. (0.1% W/v). Dissolve 0.1g ANSA in 50 ml absolute methanol. Dilute to 100 ml with absolute methanol in a volumetric flask. Mix. Keep stoppered, when not in use, to minimize evaporative losses. Prepare fresh daily. (CAUTION: Older reagent may result in lower absorbance).

6.2.10 Standard Nitrite Solution. Dissolve sufficient desiccated sodium nitrite and dilute with distilled water to 1000 ml so a solution containing 1000 $\mu\text{gNO}_2^-/\text{ml}$ is obtained. The amount of NaNO_2 to use is calculated as follows:

$$G = \frac{1.500}{A} \times 100$$

where

G = Amount of NaNO_2 , grams.

1.500 = Gravimetric factor in converting NO_2 into NaNO_2

A = Assay, percent

7. Procedures

7.1 Sampling. Assemble the sampling apparatus, as shown in Figure D-1. Components upstream from the absorption tube may be connected, where required, with teflon or polypropylene tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with tygon, teflon or polypropylene. Add exactly 50 ml of absorbing reagent to the calibrated absorption tube

(8.1.3). Disconnect funnel, insert calibrated flowmeter (8.1.1) into the end of the probe and measure flow before sampling. Denote as F_1 . If flow rate before sampling is not between 180-220 cm^3/min replace the flow controlling device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range. Sample for 24-hours and measure the flow after sampling by again inserting a calibrated flowmeter into the probe, after removing the funnel. Denote as F_2 .

7.2 Analysis. Replace any water lost by evaporation during sampling by adding distilled water up to the calibrated mark on the absorption tube. Mix well. Pipet 5 ml of the collected sample into a test tube, add 0.5 ml of the peroxide solution and mix vigorously for approximately 15 seconds. Add 2.7 ml of sulfanilamide solution and mix vigorously for about 30 seconds. Then pipet 3 ml of the ANSA solution, mix vigorously for about 30 seconds. The ANSA must be added within 6 minutes of mixing the sulfanilamide solution. (CAUTION: Longer time intervals will result in lowered absorbance values). Prepare a blank in the same manner using 5 ml of unexposed absorbing solution. The absorbance of the blank should be approximately the same as the y-intercept in the calibration curve (Section 8.2). Determine absorbance at 550 nm with distilled water in the reference cell using 1 cm cells. The color can be read anytime from 1 to 40 minutes after addition of the ANSA. Read $\mu\text{g NO}_2^-/\text{ml}$ from the calibration curve (Section 8.2).

7.3 Spectrophotometer cells must be rinsed thoroughly with distilled water, acetone, and dried, otherwise a film will build up on the cell walls.

8. Calibration and Efficiencies

8.1 Sampling

8.1.1 Calibration of Flowmeter. (See Figure D-2.) Using a wet test meter and a stopwatch, determine the rates of air flow (cm^3/min) through the flowmeter at a minimum of four different ball positions. Plot ball position versus flow rate.

8.1.2 Flow Control Device. The flow control device results in a constant rate of air flow through the absorbing solution and is determined in 7.1.

8.1.3 Calibration of Absorption Tube. Calibrate the polypropylene absorption tube, (Section 5.1.2) by first pipeting in 50 ml of water or absorbing reagent. Scribe the level of the meniscus with a sharp object, go over the area with a felt-tip marking pen, and rub off the excess.

8.2 Calibration Curve. Dilute 5.0 ml of the $1000 \mu\text{g NO}_2^-/\text{ml}$ solution to 250 ml with absorbing reagent. This solution contains $20 \mu\text{g NO}_2^-/\text{ml}$. Dilute 5.0 ml of the $20 \mu\text{g NO}_2^-/\text{ml}$ standard to 200 ml with absorbing reagent. This solution contains $0.50 \mu\text{g NO}_2^-/\text{ml}$. Prepare calibration standards by pipeting the indicated volume of the standard into volumetric flasks and diluting to the mark with absorbing reagent.

<u>Volume of Standard</u>	<u>Final Volume ml</u>	<u>Concentration $\mu\text{g NO}_2^-/\text{ml}$</u>
10 ml of $0.50 \mu\text{g NO}_2^-/\text{ml}$	100	0.05
20 ml of $0.50 \mu\text{g NO}_2^-/\text{ml}$	100	0.10
2 ml of $20 \mu\text{g NO}_2^-/\text{ml}$	200	0.20
Use $0.50 \mu\text{g/ml}$ Standard Directly	—	0.50
5 ml of $20 \mu\text{g NO}_2^-/\text{ml}$ Standard	100	1.00
9 ml of $20 \mu\text{g NO}_2^-/\text{ml}$ Standard	100	1.80

Run standards, plus a blank, as instructed in 7.2. Plot absorbance vs $\mu\text{g NO}_2^-/\text{ml}$. A straight line should be obtained with a slope of approximately 0.5₀ absorbance units/ $\mu\text{g NO}_2^-/\text{ml}$, and a y-intercept (i.e., zero $\mu\text{g NO}_2^-/\text{ml}$) of approximately 0.01 absorbance units. The absorbance is linear up to a concentration of 4.0 $\mu\text{g NO}_2^-/\text{ml}$, absorbance of 1.9. Therefore, if samples exceed the absorbance of the highest calibration standard and the above absorbance is within the range of the spectrometer, the calibration curve can be extended by including higher concentration standards. If a higher absorbance range is not available, samples must be diluted with absorbing reagent until the absorbance is within the range of the highest standard.

8.3 Efficiencies. An overall average efficiency of 93% was obtained from test atmospheres having a nitrogen dioxide concentration of 20 to 700 $\mu\text{g}/\text{m}^3$.

9. Calculation

9.1 Sampling

9.1.1 Calculate volume of air sampled.

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6}$$

V = Volume of air sampled, m^3 .

F_1 = Measured flow rate before sampling, cm^3/min .

F_2 = Measured flow rate after sampling, cm^3/min .

T = Time of sampling, min.

10^{-6} = Conversion of cm^3 to m^3 .

9.1.2 Uncorrected Volume. The volume of air sampled is not corrected to S.T.P., because of the uncertainty associated with 24-hour average

temperature and pressure values.

9.2 Calculate the concentration of nitrogen dioxide as $\mu\text{g NO}_2/\text{m}^3$.

$$\mu\text{g NO}_2/\text{m}^3 = \frac{(\mu\text{g NO}_2/\text{ml}) \times 50}{V \times (0.93)}$$

50 = Volume of absorbing reagent used in sampling, ml.

V = Volume of air sampled, m^3 .

0.93 = Overall efficiency of method.

9.2.1 If desired, concentration of nitrogen dioxide may be calculated as ppm NO_2 .

$$\text{ppm} = (\mu\text{gNO}_2/\text{m}^3) \times 5.32 \times 10^{-4}$$

10. References

1. Malik, J. D., Fuerst, R. G., Meeker, J. R., Guyer, H., Sawicki, E.
"A Twenty-Four Hour Method for the Collection and Manual Colorimetric Analysis of Nitrogen Dioxide. Presented at the 165th ACS National Meeting in Dallas, Texas, April 8-13, 1973.
2. Lodge, J. P., Jr., Page, J. B., Ammons, B. E., Swanson, G. A. "The Use of Hypodermic Needles as Critical Orifices in Air Sampling." J.A.P.C.A. 16, 197-200 (1966).

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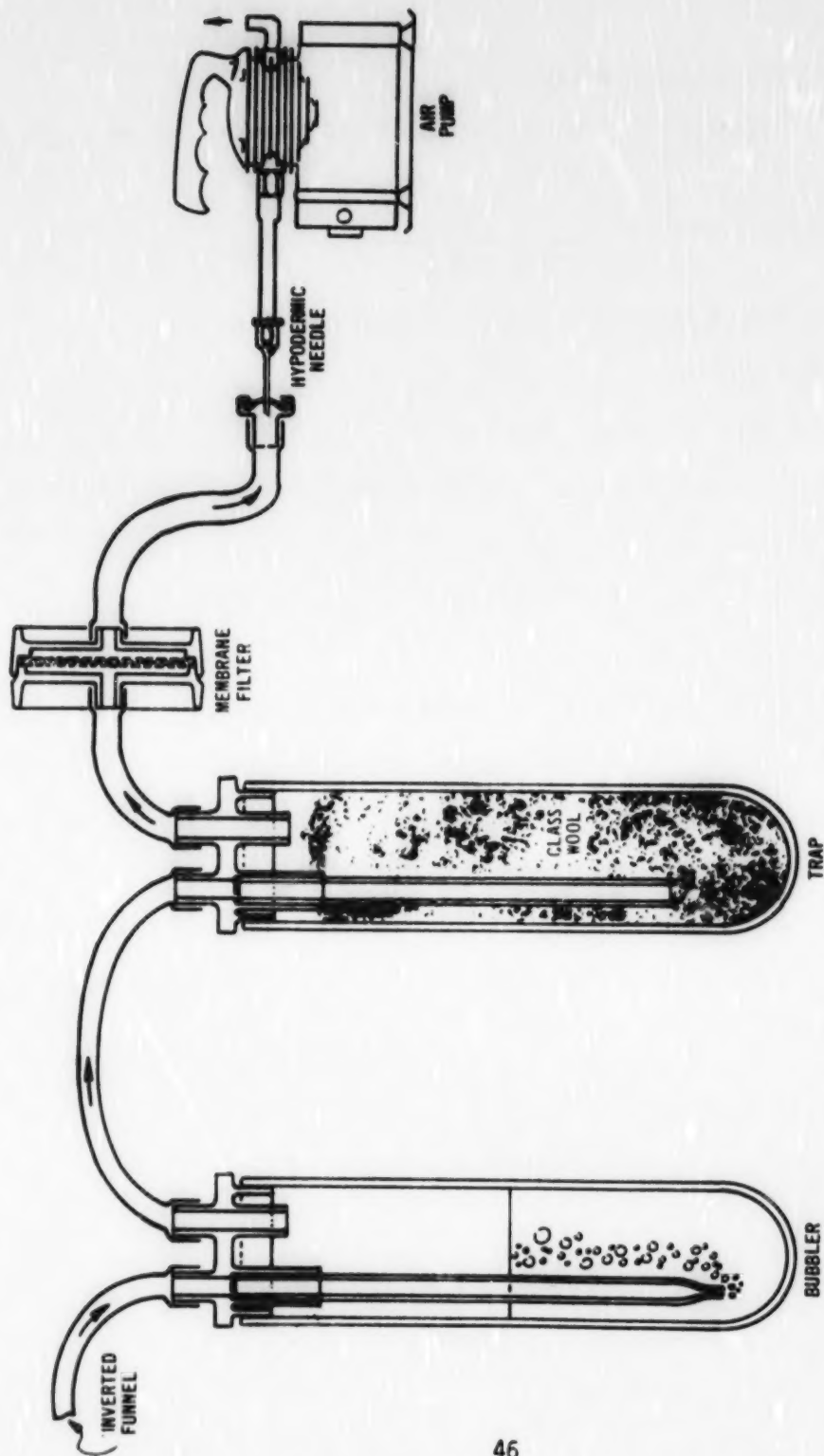


Figure D-1. Sampling train.

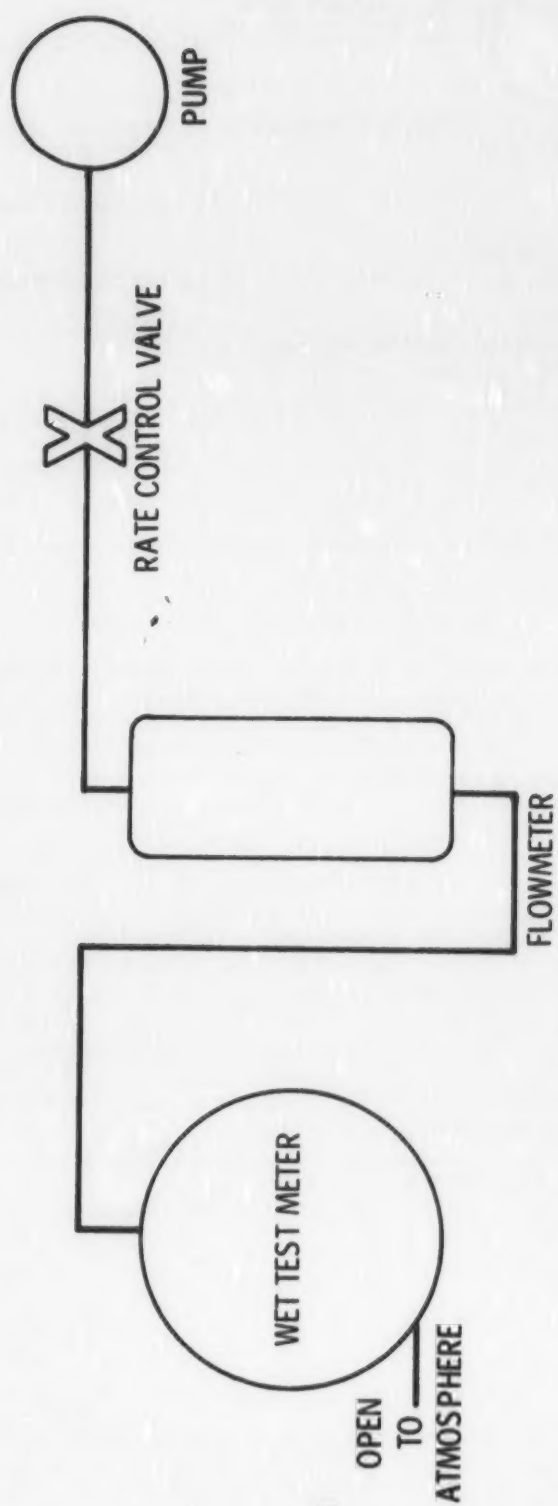


Figure D-2. Flowmeter.